

HIGH-SURFACE-AREA HYDRATED LIME FOR SO₂ CONTROL

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KEYWORDS: SO₂ removal, hydrated lime, dry sorbent injection

INTRODUCTION

For many site specific applications, dry sorbent injection technologies offer advantages over the wet flue gas desulfurization systems for controlling the emissions of SO₂ produced during combustion of high sulfur coal. These potential advantages include ease of retrofit, dry waste, and lower capital investment. The technologies that have been researched considerably in recent years include furnace sorbent injection (FSI), boiler economizer injection, and post furnace duct-injection/humidification (Coolside). The main factor which distinguishes the dry processes is that a calcium-based sorbent is injected into different locations within a pulverized coal boiler unit. In the FSI, limestone (CaCO₃) or hydrated lime (Ca(OH)₂) is injected into the upper furnace cavity where temperatures range from 1800-2200°F. The sorbent is rapidly calcined forming CaO which reacts with SO₂ to form CaSO₃. In the boiler economizer process, Ca(OH)₂ is injected in a location between the superheater and air preheater where the temperature is in the range of 800-1200°F.¹ Coolside desulfurization involves Ca(OH)₂ injection in the duct work downstream of the air preheater at about 300°F followed by flue gas humidification with a water spray.² SO₂ is removed by the entrained sorbent particles in the duct work and by the dense sorbent bed collected in the particulate removal system. Unlike the FSI where CaSO₃ is formed, under boiler economizer and Coolside conditions CaSO₃ is the major product.

Bench- and pilot-scale tests have shown that typical SO₂ capture efficiencies under FSI conditions are about 35 and 55% for CaCO₃ and commercial Ca(OH)₂, respectively,^{3,4} and 30-50% with commercial Ca(OH)₂ under boiler economizer and Coolside conditions⁶ (all at Ca/S ratio of 2). In some Coolside process pilot tests, an additive such as sodium hydroxide or sodium carbonate has been injected with the humidification water resulting in SO₂ removal of about 70 to 80%.^{6,11} Because these SO₂ removal levels correspond to less than 50% of the theoretical saturation capacity for the sorbents, a major objective of research in the recent years has been to identify sorbent properties that result in enhanced SO₂ capture in order to reduce operating costs and the amount of waste products. In FSI studies, the superiority of Ca(OH)₂ over CaCO₃ has been attributed to the smaller mean particle size,⁵ higher surface area and porosity,⁸ larger pores⁹ and plate-like grain structure¹⁰ (vs. sphere-like) of the CaO derived from Ca(OH)₂ compared to that derived from CaCO₃. In boiler economizer and Coolside studies, improved SO₂ removal performance has also been reported for Ca(OH)₂ with high porosity, high surface area, and small particle size.^{1,5,11}

This paper reviews recent work comparing the SO₂ removal performance of two commercial hydrated limes and a high-surface-area (HSA) hydrated lime under FSI, boiler economizer, and Coolside conditions. The properties of the sorbents and a discussion of the results are presented.

EXPERIMENTAL

Test Sorbents

The sorbents tested included a HSA hydrate and two commercial hydrated limes designated as A and B. The HSA hydrate and commercial hydrate A were made from the same lime. The HSA hydrated lime was prepared by a proprietary hydration process developed at the

Illinois State Geological Survey. Three hundred pounds of the sorbent was prepared using a bench-scale hydrator capable of producing seven pounds of products per batch. The HSA hydrate was not subjected to air classification or milling prior to being tested for sulfur removal efficiency.

Chemical compositions of sorbents were determined by X-ray fluorescence. Surface areas were obtained by N_2 -adsorption in conjunction with the one point BET method. Pore volumes and pore size distributions (pores smaller than 0.25 micrometers) were determined by nitrogen porosimetry. Sorbent particle size analyses were performed on a Micromeritics sedigraph 5100 using Micromeritics dispersant. Hydrate A and the HSA hydrate were examined by X-ray diffraction (XRD) and the data were used for determination of crystallite size using the Scherrer equation.¹²

Pilot-Scale SO_2 Removal Tests

FSI tests - These experiments were performed in the Innovative Furnace Reactor (IFR) located at the U. S. Environmental Protection Agency, Research Triangle Park, North Carolina.¹³ FSI tests were performed burning four Illinois coals from the Illinois Basin Coal (IBC) Sample Program. The analyses of the coals identified as IBC-101, -102, -106 and -109 are presented in table 1.

Testing in the IFR consisted of determining the SO_2 concentration in the flue gas during sorbent injection while burning each of the coals at feed rates sufficient to yield a thermal rating of approximately 14 kW. The tests were conducted with HSA hydrate and hydrate A at Ca/S ratios of approximately 1:1 and 2:1 and at a temperature of 2192°F. The details of test procedures and a description of the IFR are given elsewhere.¹³

Boiler economizer tests - The Research-Cottrell Environmental Services and Technologies (R-C EST) 150 kw pilot-scale furnace located in Irvine, California was used for boiler economizer tests. The experiments were conducted at a nominal input rate of 75 kw. A detailed description of the unit is given elsewhere.⁵ The furnace is fired on natural gas and SO_2 is added at the proper concentration. A time-temperature history representative of a utility boiler backpass is generated by using the upper section of the furnace to reduce the flue gas temperature to approximately 1300°F. The gas temperature is then decreased from 1300 to 800°F in approximately 0.5 seconds in the section of the furnace where convective tube banks are located. The flue gas is continuously analyzed for oxygen, sulfur dioxide and carbon dioxide using the R-C EST continuous emissions monitor (CEM).

The test program involved testing HSA hydrate and hydrate A at injection temperatures of 900, 1000 and 1100°F, a Ca/S ratio of 2, and SO_2 concentrations of 500 and 3000 ppm. The flue gas composition was typically 4.0% O_2 , 9.8% CO_2 , and 50 ppm CO.

Coolside tests - These tests were conducted in a 100 kW pilot unit located in the Research and Development Department of the Consolidation Coal Company, Liberty, Pennsylvania. The Coolside pilot plant is described elsewhere.² Briefly, the exhaust from a natural gas burner is mixed with recycle gas, into which CO_2 , SO_2 , N_2 , steam and fly ash are injected to produce the simulated flue gas from a coal-fired boiler. The humidifier is an 8.3-inch ID down-flow duct installed with a water-spray nozzle, and is 20 feet long from the nozzle location to the exit. The gas exiting the humidifier enters a baghouse which separates the solids from the gas. The gas is further cooled and dehumidified in a condenser, and the process fan recycles most of the flue gas for reuse. SO_2 removal is calculated from measurements of SO_2 and O_2 analyzers at the humidifier inlet and exit, and the baghouse exit.

HSA hydrated lime and hydrate B were tested at Ca/S ratios of 0.5 to 2.0 and 25°F approach to adiabatic saturation temperature. The conditions selected represent standard pilot plant tests for evaluating a new sorbent to provide SO₂ removal data at typical Coolside in-duct injection operating conditions. The common conditions were 300°F inlet flue gas temperature, 1500 ppm inlet SO₂ content (dry basis), and 125°F adiabatic saturation temperature. The flue gas flow rate was set at 175 scfm, which provided a 2.0 sec humidifier residence time.

RESULTS AND DISCUSSION

Test Sorbents

The chemical and physical properties of hydrates A and B, the HSA hydrate and lime A (from which hydrate A and the HSA hydrate were made) are presented in table 2. In the FSI and boiler economizer systems, the HSA hydrated lime was tested against the hydrate A. However, in the Coolside tests, HSA hydrate was tested against hydrate B, since this material has been shown to be the best-performing commercial sorbent under Coolside conditions.

Chemical analyses of hydrated limes indicate that the sorbents contained over 96 wt% CaO after ashing. The mass mean diameters and surface areas of the HSA hydrated limes varied between 1.6 and 2.7 micrometers and 35 to 44 m²/g (except for one batch which was 31 m²/g), respectively, depending on the hydration batch. These samples, however, had surface areas well above the 20-23 m²/g surface areas typical for commercial hydrates. The pore volume of the HSA hydrate was 0.35 cm³/g compared to only 0.08 cm³/g for its commercial counterpart. The XRD results showed that the HSA hydrate had smaller Ca(OH)₂ grain size and lower crystallinities when compared to commercial material.

Pilot-Scale SO₂ Removal Tests

FSI tests - The results for FSI tests are presented in table 3. The average baseline SO₂ concentrations under the test conditions were 3140 ppm for IBC-101, 2410 ppm for IBC-102, 2890 ppm for IBC-106 and 1000 ppm for IBC-109. The trend in the SO₂ concentration is consistent with the total sulfur content of the coals reported in table 1. Figure 1 shows the estimated SO₂ removal percentages at Ca/S ratio of 2. The values were calculated by extrapolating linearly from the mean removals at both Ca/S ratios run for each coal/sorbent combination. For each coal tested, HSA hydrate removed more SO₂ than its commercial counterpart. SO₂ removal observed with the HSA hydrate ranged from 72 to 77% for the coals tested (excluding IBC-102) compared to 55 to 66% for hydrate A.

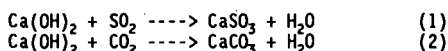
The SO₂ capture levels for the IBC-102 coal were only 57 and 42% with the HSA and commercial hydrates, respectively. The substantial decrease in SO₂ capture by the sorbents for this coal could be related to its higher pyritic sulfur content than for the other coals tested. The pyritic/organic sulfur ratio for IBC-102 was 2.3:1 compared to values less than 1:1 for the other coals. One explanation that could be offered is that a major fraction of the organic sulfur in coals is released as H₂S in the initial stages of the combustion and is rapidly captured by the fresh sorbent. The SO₂ released by the oxidation of the pyrite, which follows the pyrolysis stage, then reacts with the partially utilized sorbent at a much slower rate compared to the H₂S reaction.¹⁴ Therefore, sulfur capture by the sorbent is lowered when coal with a high concentration of pyritic sulfur is burned. This suggests that FSI is most beneficial for coals that are high in organic sulfur which cannot be removed by physical coal cleaning.

The enhanced performance of the HSA hydrate could be related to its smaller particle size and higher initial surface area. Laboratory tests conducted under FSI conditions at 2012°F with CaO derived from Ca(OH)₂ have revealed that the CaO conversion to CaSO₃ is inversely related to particle diameter to the 0.2 to 0.35 power⁷. In a recent study, however, the initial sulfation rate of CaO (7 to 100 micrometers) derived from several limestones and dolomites varied roughly inversely with the particle size, indicating pore diffusion was the rate controlling step under these test conditions (1650°F). Based on the data obtained in this work, SO₂ capture was inversely related to particle size to the 0.44 power (for capture values estimated at Ca/S ratios of 1 and 2).

The higher SO₂ capture of the HSA hydrate can also be attributed in part to its favorable pore structure. Pore volume analyses of raw sorbents, shown in figure 2, indicate the volume of pores between 0.01 and 0.1 micrometers (10 and 100 nm) is substantially higher for the HSA hydrate than for hydrate A. Pore volumes of hydrated limes are expected to correlate with pore volumes of the corresponding calcines. Due to the increase in molar volumes when converting from CaO to CaSO₃ (16.9 vs 46.0 cm³/mole), pore plugging is known to limit the sulfation reaction. Therefore, sorbents with a high volume of larger pores are expected to capture more SO₂.

Boiler economizer tests - The results of these experiments are shown in figure 3. The HSA hydrate showed significantly greater SO₂ removals than hydrate A at all test conditions. The SO₂ reduction achieved with the HSA hydrate at 3000 ppm SO₂ and Ca/S of 2 was 58% at 900°F, 57% at 1000°F and 52% at 1100°F compared to only 32%, 30% and 28% for the commercial hydrate. At 500 ppm SO₂ and Ca/S ratio of 2, the average SO₂ removals for hydrate A and the HSA hydrate were 6.1 and 17%, respectively (an increase of 180%). The SO₂ removals observed for the HSA hydrate were also higher than for other commercial hydrates examined under similar test conditions.⁵

The superior performance of the HSA hydrate observed in this study is attributed, in part, to its high surface area and small particle size. The role of surface area and particle size can be explained in terms of two competing reactions under boiler economizer conditions,



The intrinsic rates (which are related to pore surface area of sorbent) of reactions (1) and (2) are very fast even at 900°F. However, because of the low concentration of SO₂ in the flue gas, reaction (1) is controlled by bulk diffusion of SO₂ for particles larger than 5 micrometers^{1,3} (diffusion rate for spherical particles is inversely related to particle size to the second power), whereas reaction (2) is controlled by intrinsic rate. As a result, the relative rates for the reaction of CaSO₃ and CaCO₃ depend both on pore surface area and particle size of the sorbent. Increasing pore surface area would favor the carbonation reaction if particle diameter is held constant. Decreasing particle size and holding pore surface area constant would favor desulfurization reaction. Therefore, a sorbent with high pore surface area and small particle size would be expected to show high SO₂ removal efficiency under boiler economizer conditions. The average increase in sulfur capture observed for the two sorbents at 3000 ppm SO₂ and Ca/S ratio of 2 was 83%, which corresponds approximately to the difference in surface areas. However, at 500 ppm SO₂ and Ca/S ratio of 2, SO₂ captures were inversely related to particle diameter to the second power, indicating bulk diffusion limitation under these test conditions.

Coolside tests - Three different batches of HSA hydrate were examined in the Coolside pilot unit. The surface areas of the samples tested at Ca/S ratios of 0.54, 1.1 and

2.1 were 31, 34 and 39 m²/g, respectively. Figure 4 shows the effect of the Ca/S molar ratio on SO₂ removal at 25°F approach to saturation. The value shown for hydrate B at 2.1 Ca/S was obtained in this study. The removals shown for the same hydrate at 1.0 and 1.5 Ca/S are from Reference 2. The HSA hydrated lime showed higher SO₂ removals than the best-performing commercial hydrate. With the HSA hydrate at Ca/S ratios of 0.54, 1.1 and 2.1, the SO₂ removals were 15, 25 and 46% in the humidifier and 18, 33 and 56% across the entire system (humidifier + baghouse). Comparison of the data at Ca/S of 2.1 indicate that the HSA sorbent captured 35% more SO₂ than hydrate B in the humidifier and 15% more across the entire system. The maximum percent calcium utilizations for the HSA hydrate were 33.3, 31.7 and 26.3 as Ca/S ratio increased from 0.54 to 2.1. For hydrate B a 23.2% utilization was observed at Ca/S ratio of 2.1.

Figure 4 shows a linear SO₂ removal behavior at the Ca/S ratios tested. Normally, as is exhibited by hydrate B, a plot of SO₂ removal vs Ca/S ratio is curved because the effect diminishes as the Ca/S ratio increases. The straight-line behavior for the HSA hydrate may be due to the sample surface area variations mentioned above.

The Coolside data suggest that a major fraction of the SO₂ capture occurred during the two second residence time in the duct work. The higher SO₂ capture achieved by the HSA hydrate in the humidifier section and across the entire system suggests higher overall activity of the sorbent relative to hydrate B.

SUMMARY AND CONCLUSIONS

The HSA hydrated lime prepared by a proprietary process had considerably higher surface area and porosity, smaller particle size, and finer Ca(OH)₂ grain size than typical commercial hydrated lime. The results of the pilot-scale testing under FSI, boiler economizer, and Coolside conditions indicate that the HSA hydrated lime removed, depending on the test system, 15-180% more SO₂ than the commercial hydrated limes tested under similar conditions. The superior performance of the HSA hydrate was attributed to its favorable physical properties.

ACKNOWLEDGEMENTS

This work was funded in part by grants from the Illinois Coal Development Board through the Center for Research on Sulfur in Coal. Dr. Brian K. Gullett of the U. S. Environmental Protection Agency provided the FSI data.

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Table 1. Average analyses of the coals (moisture free values).^{1,2}

	IBC-101	IBC-102	IBC-106	IBC-109
Moisture	14.8	14.3	10.5	9.2
Vol Matter	40.7	39.9	39.7	35.0
Fixed Carbon	48.8	53.3	51.3	56.8
H-T Ash	10.5	6.8	9.0	8.2
Carbon	69.30	74.10	71.86	75.05
Hydrogen	5.18	5.32	4.93	4.89
Nitrogen	1.31	1.50	1.67	1.74
Oxygen	9.31	8.92	8.76	8.53
Sulfatic Sulfur	0.05	0.06	0.01	0.00
Pyritic Sulfur	1.22	2.26	1.86	0.50
Organic Sulfur	3.08	0.98	1.90	0.63
Py/Or Ratio	0.40	2.30	0.98	0.80
Total Sulfur	4.36	3.30	3.77	1.13
Total Chlorine	0.12	0.02	0.02	0.42
Btu/lb	12659	13628	13226	13324

¹ All values in wt% except where noted

² Analyses were performed by LECO analyzers and are different than those obtained by the ASTM methods and reported in reference 13.

Table 2. Properties of test sorbents

Sorbent	Ash Analyses, (wt%)		Mean diameter (micrometers)	BET surface area (m ² /g)	Pore volume ¹ (cm ³ /g)	Crystallite size (angstroms)
	CaO	MgO				
Lime A	96.1	0.52	---	1.6	---	---
Hydrate A	99.0	0.57	3.5	20.6	0.08	220
HSA hydrate	96.5	1.20	2.0 ²	38.0 ³	0.35	150
Hydrate B	97.7	0.55	3.1	23.2	---	---

¹ Pores smaller than 0.25 micrometers.² The value is an average. The range was 1.6 to 2.7 micrometers.³ The value is an average. The range was 35 to 44 m²/g.Table 3. Furnace Sorbent Injection (FSI) data.¹

Coal (%)	Sorbents Ca/S	Baseline SO ₂	Removal (ppm)	Ratio
IBC-101	Hydrate A	3161	28.8	0.85
	Hydrate A	3161	56.6	1.70
	HSA hydrate	3120	36.6	0.79
	HSA hydrate	3120	61.4	1.58
IBC-102	Hydrate A	2541	25.6	0.88
	Hydrate A	2541	42.1	1.75
	HSA hydrate	2288	32.8	0.85
	HSA hydrate	2288	50.3	1.70
IBC-106	Hydrate A	2918	36.5	1.10
	Hydrate A	2918	63.7	2.21
	HSA hydrate	2862	59.8	1.07
	HSA hydrate	2862	78.7	2.14
IBC-109	Hydrate A	1032	40.8	0.92
	Hydrate A	1032	52.7	1.84
	HSA hydrate	960	47.1	1.16
	HSA hydrate	960	80.6	2.32

¹ Data from reference 13.

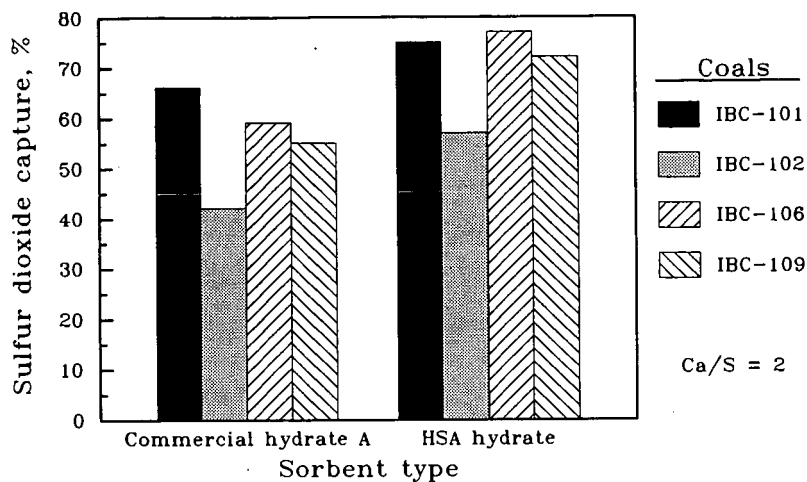


Figure 1. Furnace sorbent injection pilot-plant data

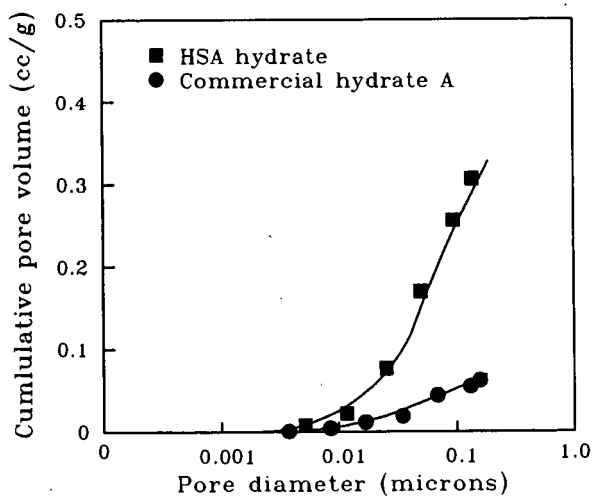


Figure 2. Pore size distribution data

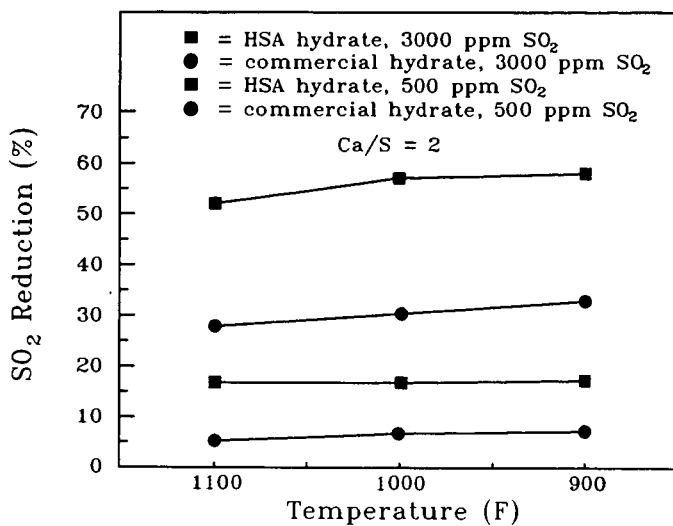


Figure 3. Boiler economizer pilot-plant data

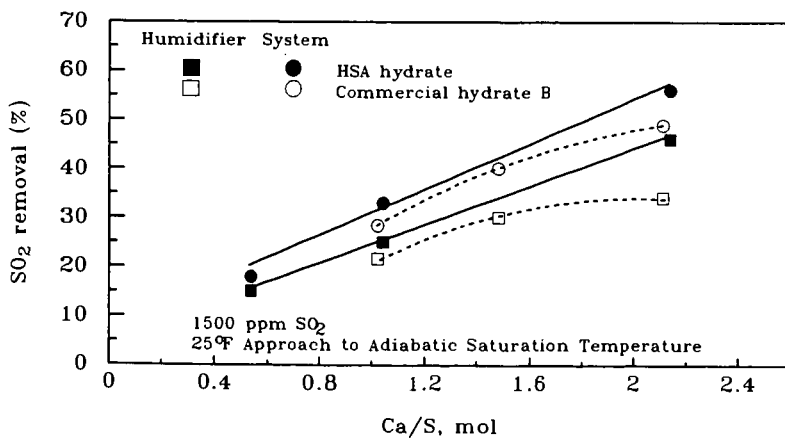


Figure 4. Coolside pilot-plant data